TITLE

PRESERVATION OF PAPER AND TEXTILE MATERIALS

FIELD OF THE INVENTION

The present invention relates to the preservation of paper articles (e.g., books, manuscripts, documents) and textiles articles (e.g., paintings on canvas, clothing, etc.) through the application of an amorphous fluoropolymer by, for example, spraying, dipping or brushing the article to be preserved with a solution of the fluoropolymer.

BACKGROUND

Commonly owned and copending PCT International Application No. PCT/US98/26903 discloses coating a substrate (e.g., a metal, ceramic or composite) including the application of a fluoropolymer solution to seal pores.

The use of fluoropolymer dispersions to coat and protect paper and fabrics is known (see e.g., U.S. Patent Nos. 4,742,140 and 5,674,961). Generally, these dispersions are comprised of particles in the neighborhood of 80 to 400 nm in diameter in an aqueous medium. The particles are not intended to fully or uniformly coat the fibers of paper or fabric. Also, because they are generally aqueous dispersions, items containing water-soluble dyes would be damaged by contact with water.

SUMMARY OF THE INVENTION

The present invention provides a method for strengthening a paper or textile article, comprising the steps of (a) applying to the article a solution of an amorphous fluoropolymer in a perfluoroalkane solvent; and (b) drying the article so that the solvent is essentially removed.

The present invention also relates to a strengthened paper or textile article comprising (i) a fibrous paper or textile substrate and (ii) amorphous fluoropolymer interconnecting fibers of said substrate.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 represents a plot of data from Table 1.

DETAILED DESCRIPTION

The present invention employs amorphous fluoropolymers which, for application, are dissolved in a perfluoroalkane solvent. Articles to be preserved are treated with the fluoropolymer solution by any suitable method, including but not limited to dipping, spraying and brushing. The article may be, but is not limited to, a book, manuscript, paper, fabric, article of clothing, painting, and the like. Normally, the amorphous fluoropolymer is used substantially transparent, and consequently there is no substantial difference in appearance between the treated article and the untreated article.

When fluoropolymer is deposited from solution onto a non-porous surface, a coating of about 5 to 20 μm thick typically results. This thickness is related to the concentration of the solution used in the deposition. Generally, a 1% solution will produce a film about 5 μm thick, and a 6% solution yields a film thickness of about 50 μm. However, when the object on which the fluoropolymer is deposited is fibrous or porous, the fluoropolymer penetrates into the object. Commonly owned and copending PCT International Application No. PCT/US98/26903 and U.S. Patent Application Serial No. 215,441 describe the penetration of fluoropolymer solutions into pores in thermal spray coatings which are used for corrosion protection. Fluorine x-ray fluorescence micrographs were used to demonstrate fluoropolymer penetration into the pores.

Useful herein are solutions of fluoropolymers with molecular weights in the range of from 200,000 to 400,000. These fluoropolymers are known to have excellent chemical resistance; and their solutions generally have relatively low viscosities (on the order of about 60 to 300 centipoise at shear rates from about 50 to 300 sec^{-1}) which enables them to flow into the pores. The location of the fluoropolymer in the pores is also important because, unlike purely surface films, the material is not easily abraded or worn away. Rather, the fluoropolymer in the pore is protected from abrasion by the surrounding porous coating as well as any surface coating. Moreover, the fibers of the substrate are interconnected with fluoropolymer, thereby strengthening the article.

Treating paper with fluoropolymer solutions can significantly increase the tensile strength of paper, as shown in Example 2 below, as well as typically impart other desirable properties. The films or deposits have very low surface energies compared to untreated paper (e.g., in the range of 15 to 19 dynes/cm). Thus, they are generally difficult to wet with liquids such as water. Solid deposits like dirt, dust or inks will not easily adhere to such surfaces. The permeation of aggressive chemical constituents of the environment which may degrade or corrode the object is retarded, as the solutions penetrate into the bulk of the material as well as depositing on the surface. Finally, the fluoropolymer film or deposit itself is very inert to degradation from environmental chemicals.

One use for this invention is the preservation of a variety of papers, including books, newspaper pages and documents. As paper ages, it frequently becomes more brittle. This is a problem for historic books and documents of great age. Treatment of these papers with the fluoropolymer solutions, as described in this invention, have been shown to increase the tensile strength of the paper, as shown in the Examples below. As outlined in Examples 1 and 2 below, a paper or book can be dipped into the fluoropolymer/perfluoroalkane solution and air dried

Minneapolis, MN). In general, the perfluoroalkane solvents used in these solutions are not considered aggressive to many paper and textile articles. Most inks will not dissolve in perfluorinated solvents. Similarly, many substrates are unaffected by exposure to these solvents.

The fluoropolymer solutions may be applied to the fibrous articles by common coating methods, including but not limited to spray application, dipping and brushing. After application of the solutions, the articles can be dried by conventional methods (e.g., air or vacuum drying).

EXAMPLES

Fluoropolymer Solution Preparation:

Teflon® AF solutions were used in the examples below, and were used as received from E. I. du Pont de Nemours and Company, Wilmington, DE, unless otherwise noted. To dilute the Teflon® AF2130, solvent (FC-75, 3M, Minneapolis, MN) was weighed and was placed into a container, with the calculated amount of Teflon® AF2130 added to the solvent. The samples were mixed before use.

EXAMPLE 1

Paper Treatment

Several types of paper, including newsprint and copier paper were dipped for about 30 seconds into several Teflon® AF solutions, having concentrations between 1 and 6% solids by weight, such that about half the sheet was impregnated with the solution. The papers were removed from the solution and dried for about 30 minutes. The entire sheets of paper were immersed in water at room temperature. The treated portion emerged in undamaged condition while the untreated paper fell apart. No dissolution or blurring of ink was observed in the treated portion of the newsprint.

EXAMPLE 2

Strength Testing of Paper

The strength of treated paper was compared to that of an untreated paper. Strips of paper (20 pound White Wove, Gilbert, Inc., Menasha, WI) about 1 inch wide, 8 inches long, and 0.004 inches thick, were immersed for 10 minutes in solutions with varying concentrations of fluoropolymer. The strips were removed and dried, leaving a fluoropolymer deposit in the paper. The tensile strengths of the strips were measured using a model 1122 Instron test machine (Instron Corp., Canton, MA) and ASTM Method D 828 procedures (the test bars were held in grips with a separation of 5 inches, and the cross head speed was 2 inches/minute). The fluoropolymer treatment increased the strength of the paper. The results are shown in Table 1 below, as well as in Figure 1.

TABLE 1

Fluoropolymer Solution Identification	Concentration of Fluoropolymer, %	Strength, Ksi	% Increase in Strength vs. Control
None	0	6.38	---
TEFLON® AF1600	3	7.42	16.3
TEFLON® AF1601	6	8.14	27.6
TEFLON® AF2400	1	7.09	11.1
TEFLON® AF2130	6	8.60	34.8
TEFLON® AF2130	3	8.55	34.0
TEFLON® AF2130	1	6.94	8.8